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(54) Process for the preparation of silver halide emulsion.

(57) A process for the preparation of a silver halide emulsion comprising silver halide grains dispersed in a dispersing medium. The process comprises the steps of (1) forming host silver halide nuclei in the dispersing medium, (2) adding a halide solution to the silver halide nuclei to form a crystal defect which gives rise the formation of tabular grain, by forming at least one gap interface of halide composition in the nuclei by a halogen conversion reaction and (3) growing silver halide grains preferentially along the direction of edges of the grains to form tabular grains having an aspect ratio (diameter per thickness) of not less than 1.5 and {100} major faces. A difference in chloride content or bromide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 10 to 100 mol % or a difference in iodide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 5 to 100 mol %.

FIG. 3

(a)

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(3.10/3.09/3.3.4)

FIELD OF THE INVENTION

The present invention relates to a process for the preparation of silver halide emulsion useful in photography. In more detail, the invention relates to a process for the preparation of a silver halide emulsion containing tabular silver halide grains that have {100} major faces.

BACKGROUND OF THE INVENTION

A tabular silver halide emulsion can be advantageously used in a photographic material. Tabular silver halide grains are generally superior to other non-tabular grains. For example, the tabular grains are improved in the spectral sensitivity, the light-scattering character, the covering power and the development property. Further, a photographic material containing the tabular grains can form an image improved in sharpness and graininess. The tabular grains usually have parallel twinned faces that are {111} major faces.

By the way, silver halide grains having {100} major faces usually have spectral sensitivities superior to those of the grains having {111} major faces in the case that a large amount of a spectral sensitizing dye is adsorbed on the silver halide grains. Therefore, it is now required to develop tabular silver halide grains having {100} major faces. Japanese Patent Provisional Publication No. 51(1976)-88017, Japanese Patent Publication No. 64(1989)-8323 and European Patent Publication No. 0534395A1 disclose the tabular silver halide grains having {100} major faces. The major faces have a rectangular shape. However, the disclosed grains do not have a gap interface (discontinuous change) of a halide composition inside the grains. The disclosed grains have a uniform halide composition or a continuous change of a halide composition.

According to study of the present inventor, it is difficult to form tabular grains selectively from silver halide nuclei having no gap interface (discontinuous change) of a halide composition. Further, the formed tabular grains are heterogeneous. For example, the grain size distribution in the prepared emulsion is broad. Furthermore, the sensitivity of the emulsion is not satisfactory. Moreover, a photographic material containing the grains cannot form an image having a sufficient image quality such as a fine graininess.

Japanese Patent Application No. 5(1993)-96250 discloses a process of forming tabular grains from silver halide nuclei having a gap interface of a halide composition. The gap interface functions as a crystal defect for forming tabular grains. However, the crystal defects formed in the nuclei are heterogeneous. Accordingly, the reproducibility of the process is still insufficient. Further, the sensitivity of the emulsion and the graininess of the obtained image are also still insufficient. Furthermore, the spectral sensitivities of the formed grains are not sufficiently high.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for the preparation of a silver halide emulsion, which is improved in sensitivity, graininess of image and spectral sensitivity.

Another object of the invention is to improve the reproducibility of the process for the preparation of the silver halide emulsion.

The present invention provides a process for the preparation of a silver halide emulsion comprising silver halide grains dispersed in a dispersing medium, wherein the process comprises steps of:

(1) forming host silver halide nuclei;

(2) adding a halide solution to the silver halide nuclei to form a crystal defect which gives rise the formation of tabular grains, by forming at least one gap interface of halide composition in the nuclei by a halogen conversion reaction, wherein a difference in chloride content or bromide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 10 to 100 mol % or a difference in iodide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 5 to 100 mol %; and

(3) growing silver halide grains preferentially along the direction of edges of the grains to form tabular grains having an aspect ratio of not less than 1.5 and {100} major faces.

In the process of the present invention, a crystal defect in host nuclei is formed by addition of a halide solution. Accordingly, the reaction system is simple. The crystal defects are homogeneously formed in the nuclei because of the simple reaction system. Therefore, the reproducibility of the process is improved. The obtained tabular grains have a uniform grain size distribution.
Further, the sensitivity of the obtained emulsion and the graininess of the obtained image are satisfactory.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically illustrates a shape of a major face of a tabular silver halide grain.

Figure 2a and 2b schematically illustrate sectional views of tabular silver halide grains.

Figures 3a and 3b are micrographs showing tabular silver halide grains of the present invention.

Figure 4 schematically illustrates shapes of major faces of tabular silver halide grains before or after grain growth.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention prepares a silver halide emulsion, which contains tabular grains having an aspect ratio of not less than 1.5 and {100} major faces. In the prepared emulsion, at least 30 % of the grain population projected area is accounted for by the tabular grains. The projected area is measured under conditions that silver halide grains are placed on a plate while not overlapping each other and that major faces of tabular grains are arranged parallel to the surface of the plate. In the emulsion, preferably 60 to 100 % and more preferably 80 to 100 % of the of the grain population projected area is accounted for by the tabular grains. The aspect ratio (diameter per thickness) of the tabular grain is not less than 1.5, preferably not less than 2, more preferably in the range of 3 to 25 and most preferably in the range of 3 to 10.

The diameter of tabular grain corresponds to the diameter of a circle having the same area as the above-mentioned projected area of the grain, which can be observed by an electron microscope. The average diameter of the tabular grains is preferably not more then 10 μm, and more preferably in the range of 0.2 to 5 μm. The thickness of tabular grain means the distance between two major faces of the grain. The average thickness of the tabular grains is preferably not more than 0.5 μm, more preferably in the range of 0.03 to 0.3 μm, and most preferably in the range of 0.05 to 0.2 μm. The silver iodide content in the tabular grains is preferably not more than 20 mol %, and more preferably in the range of 0 to 10 mol %. The prepared emulsion preferably is monodispersed. In more detail, the distribution coefficient (standard deviation per average diameter) is preferably in the range of 0 to 0.4, more preferably in the range of 0 to 0.3 and most preferably in the range of 0 to 0.2.

The tabular silver halide grains preferably have a rectangular projected shape. Accordingly, the major faces of the grains have the rectangular shape. The rectangular shape includes the following embodiments (a) to (e).

(a) The adjacent edge ratio (the length of the long edge per that of the short edge) is 1 to 10 (preferably 1 to 5, and more preferably 1 to 2).

(b) At least one corner of the rectangular major face is irregularly rounded (which is described in Japanese Patent Application No. 4(1992)-145031 and European Patent Publication No. 0,534,395A1).

(c) At least two parallel edges of the rectangular major face are curved toward outside.

(d) A rectangular shape is chipped from at least one corner of the major face, as is illustrated in the Figure 1.

(e) The four corners of the major face are chipped almost equivalently (wherein the largest chipped area per the smallest chipped is less than 2 in the major face of one silver halide grain).

The embodiments (a), (b) and (e) are preferred. The embodiment (e) is more preferred. In the embodiment (e), the chipped area preferably has a {111} face. The area of the {111} face is preferably 0 to 40 %, and more preferably 0.5 to 20 % based on the total surface area of the tabular grain.

Next, the tabular silver halide grains formed at the step (3) is described below.

The tabular grain has at least one gap interface of halide composition. A difference in chloride content or bromide content at the gap interface is preferably in the range of 10 to 100 mol %, more preferably in the range of 30 to 100 mol %, and most preferably in the range of 50 to 100 mol %. Alternatively, a difference in silver iodide content at the gap interface is preferably in the range of 5 to 100 mol %, more preferably in the range of 10 to 100 mol %, and most preferably in the range of 30 to 100 mol %. The gap interface is substantially formed by addition of a halide salt solution to host silver halide nuclei according to a halogen conversion reaction. A difference in chloride content or bromide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 10 to 100 mol %, preferably in the range of 30 to 100 mol %, and more preferably in the range of 50 to 100 mol %. Alternatively, a difference in iodide content between the halide composiiton of the host silver halide nuclei and the halide composition of the halide solution is in the range of 5 to 100 mol %, preferably in the range of 10 to 100 mol %, and more preferably in the range of 30 to 100 mol %. A silver solution may be added simultaneously with the addition of the halide solution. The above-mentioned expression "the gap interface is substantially formed by addition of a halide salt solution" means that the ratio (a1/a2) of the molar amount of the silver solution (a1) to the molar amount of the halide solution (a2) is less than 0.9, preferably in the range of 0 to 0.3, and more preferably in the range of 0 to 0.1.

The halide solution preferably has such a halide composition that the ratio (b1/b2) of the solubility of the silver halide having the same halide composition as that of the halide solution (b1) to the solubility of the silver halide of the host nuclei (b2) is preferably less than 1, more preferably lens than 0.8, and most preferably in the range of 10^{-5} to 0.3. The halide conversion reaction can be conducted twice or more times. The reaction is preferably conducted once to four times, and more preferably conducted once or twice.

Host silver halide nuclei (AgX_1) can be formed by addition of a halide (X^- salt) solution and a silver nitrate solution to a dispersing medium while stirring. Next, another halide solution is added to the silver halide nuclei to cause a conversion reaction. Thus, grains of $AgX_1|AgX_2$ are formed. The nuclei formation can be completed at this stage. Further, a silver nitrate solution or a silver nitrate solution and a halide solution may be added to the grains of $AgX_1|AgX_2$ to form grains of $AgX_1|AgX_2|AgX_3$. Furthermore, grains of $AgX_1|AgX_2|AgX_3|AgX_4$ can be formed by addition of a halide solution according to a halide conversion reaction. The above-mentioned procedures can be further repeated. The halide composition of AgX_3 may be the same as the composition of AgX_1. Accordingly, the combination of the halide compositions can be optionally determined.

The ratio of the molar amount of the halide solution for the conversion reaction to the molar amount of the host nuclei is preferably not less than 0.01, and more preferably not less than 0.1. In the case that the nuclei have a structure of $AgX_1|AgX_2|AgX_3$, the thickness of the gap interface layer of AgX_2 is preferably thicker than the diameter of one atom. A crystal defect is formed by the conversion reaction. The tabular grain formation is based on the presence of the crystal defect in the nuclei. The grains of AgX_1 preferably have an average size of not more than 0.2 µm, and more preferably in the range of 0.02 to 0.1 µm.

The steps of the process of the present invention are described blow in more detail.

(1) Host silver halide nuclei (AgX_1) can be formed by a reaction of silver ion with a halide ion in a dispersing medium contained in water.

(2) A halide solution is added to the silver halide nuclei to cause a halide conversion reaction on the surface of the nuclei of AgX_1. Thus crystal defects that give rise the formation of tabular grains are substantially formed by the conversion reaction. The reaction conditions for the crystal defects are so adjusted that {100} faces are formed. The conditions for the {100} faces are described in Japanese Patent Application No. 5(19930-96250. The reaction solution may contain an agent for the formation of the {100} face. The amount of the agent is preferably not less than 5 %, and more preferably in the range of 10 to 300 %, based on the saturated amount of the agent adsorbed on the nuclei. The agent for adjusting crystal habit decreases the silver potential at the formation of nuclei by not less than 10 mV, and preferably by 30 to 200 mV.

The potential can be determined by measuring a potential difference between a silver ion selective electrode (e.g., silver electrode) and a saturated calomel electrode according to a potentiometric method.

In more detail, grains having the same ratio of the area of a {100} face to the area of a {111} face can be formed at a lower silver potential by using the agent for adjusting crystal habit. The agents for adjusting crystal habit are described in European Patent Publication No. 0,534,395A1. Further, a gelatin having a high methionine content is available as the agent. The methionine content is preferably not less than 10 µmol/g, and more preferably in the range of 30 to 200 µmol/g. A water-soluble dispersing agent used for a conventional silver halide emulsion is also available. The water-soluble dispersing agents are generally described in Research Disclosure, volume 307, item 307105 (November, 1989). Preferred dispersing agents are described in Japanese Patent Publication No. 52(1977)-16365, Japanese Patent Provisional Publication No. 59(1984)-8604 and Journal of Imaging Science, volume 31, pages 148 to 156 (1987).

The temperature for the nuclei formation is preferably in the range of 5 to 70 °C, and more preferably in the range of 10 to 50 °C. The grain size of the nuclei is preferably small for ripening at the next stage. On the other hand, an energy, namely a high temperature is necessary for a halide conversion reaction to cause a crystal defect. To meet the above-mentioned two requirements, the nuclei formation and the addition of the halide solution are conducted at a lower temperature, and then the temperature is raised by 2 °C or more, and preferably by 5 to 30 °C.

Thus the nuclei of $AgX_1|AgX_2$ are formed. Though the nuclei can be ripened at the next stage, a silver nitrate solution or a silver nitrate solution and a halide solution are preferably added to the grains of $AgX_1|AgX_2$ to form grains of $AgX_1|AgX_2|AgX_3$. In the grains of $AgX_1|AgX_2|AgX_3$, deposition of AgX_2 on tabular grains is inhibited at the ripening stage so that the number of crystal defects in the tabular grains is controlled. In more detail, X_2 is diluted with X_3 in the AgX_3 phase at the ripening stage to prevent the formation of the defects. The halide composition of X_1 preferably is substantially the same as the composition of X_3. The term "substantially the same" means that a difference in chloride content, bromide content or iodide content between X_1 and X_3 is not more than 30 mol %, and preferably in the range of 0 to 10 mol %. The amount of AgX_3 is preferably larger than the amount of AgX_2. The amount ratio of AgX_3 to AgX_2 is in the range of 5 to 300.

In the case that too many defects are contained in a grain, the formed grain has a thick structure having a low aspect ratio because the grain is grown along the directions of the x, y and x axes. The x and y axes are parallel to the major face, and are perpendicular to each other. The x axis is perpendicular to the major face. The number of the defects should be so controlled that the number of the thick grains is decreased and the number of the tabular grains is increased. The number of the defects is increased by increasing the gap difference in the halide composition between AgX_1 and AgX_2 or increasing the molar ratio of AgX_2 to AgX_1. The concentration of the dispersing medium is usually in the range of 0.1 to 10 wt.%. The pH is preferably in the range of 1 to 12, and more preferably in the range of 2 to 7. The crystal defect is preferably formed by a difference in the halide composition of bromide or chloride.

(3a) It is difficult to form nuclei for tabular grain selectively at the nuclei formation. Therefore, grains other than tabular grains are dissolved according to an Ostwald ripening. The temperature at the ripening is higher (preferably 10 °C or more) than the temperature at the nuclei formation. The temperature at the ripening is usually in the range of 50 to 90 °C. At the ripening, non-tabular grains disappear, and are deposited on tabular grains. Almost (preferably not less than 70 %, preferably 95 to 100 %) of the non-tabular grains can disappear by the ripening. The other methods can be used to reduce the non-tabular grains. At the ripening, silver halide of AgX_2 might be deposited on tabular grains to form many defects in the tabular grains. Accordingly, fine grains of the above-mentioned AgX_3 are preferably added to the nuclei after the nuclei formation to prevent the formation of the defects. Additionally or alternatively, a silver salt solution and a halide solution of X_3 can be added to the nuclei at the ripening stage. The amount of X_3 is preferably so adjusted that AgX_2 is diluted with AgX_3 substantially not to form new defects in the tabular grains. The term "substantially" means that the number of the new defects is not more than 50 %, preferably in the range of 0 to 20 %, and more preferably in the range of 0 to 10 %, based on the number of the previously formed defects.

The above-mentioned procedures can be employed in combination. For example, at least 10 % (preferably 20 to 95 %) of the non-tabular grains disappear at the ripening, and then the remaining non-tabular grains disappear by addition of lower supersaturated amounts of a silver salt solution and a halide solution. In another example, the tabular grains are grown preferentially along the direction of edges while adding lower supersaturated amounts of a silver salt solution and a halide solution to increase the size difference between the tabular and non-tabular grains, and then the non-tabular grains disappear at the ripening. The lower supersaturated amount means a such saturation degree that the ratio of the growth speed of grains having no defects per the growth speed of the tabular grains along the direction of the edges is not larger than 0.5, preferably not larger than 0.1, and more preferably not larger than 0.

(3b) After the above-mentioned ripening, the grains can be grown to obtain a required size. The grain growth can be conducted by addition of ions, addition of fine grains or a mixture thereof. A silver salt solution and a halide solution are used at the ion addition. Fine silver halide grains are previously formed and used at the fine grains addition.

The halide composition of the tabular grains is described in Japanese Patent Application No. 5(1993)-96250.

The tabular silver halide grains of the present invention preferably have a core/shell structure. Examples of the core/structure are illustrated in Figures 2(a) and 2(b). In the Figures 2(a) and 2(b), the core of AgX_5 preferably has a silver chloride content of not less than 60 mol %, more preferably in the range of 70 to 99.99 mol %, and most preferably in the range of 90 to 99.95 mol %. The shell of AgX_5 preferably has a silver bromide content of not less than 30 mol %, more preferably in the range of 50 to 100 mol %, and most preferably in the range of 70 to 100 mol %. The ratio of the silver chloride content in the shell to the silver chloride content in the core is preferably not larger than 0.8, more preferably in the range of 0 to 0.5, and most preferably in the range of 0 to 0.2.

It is preferred that the shell is substantially uniformly formed on the {100} major faces of the core grains. The term "substantially uniformly" means that the distribution coefficient of the thickness of the shell in a grain is not larger than 0.4, preferably in the range of 0 to 0.3, and more preferably in the range of 0 to 0.1. Further, the shell preferably has a thickness in terms of three or more atoms, more preferably 5 to 700 atoms, and most preferably 5 to 300 atoms. In other words, the thickness is preferably thicker than the thickness of layered three or more atoms. The shell may be formed on the whole surface of the core grains, as is illustrated in Figure 2(b). It is further preferred that the thickness of the shell formed on the {100} major faces is substantial uniform in each of the grains. It is furthermore preferred that the thickness of the shell formed on the whole surface of the core is substantial uniform in each of the grains. The term "substantially uniform" has the same meaning as that of the term "substantially uniformly" defined above.

The distribution coefficient of the silver bromide content in the shell of each of the grains (the ratio of the standard deviation of the silver bromide content in the shell of each of the grains to the average silver bromide content) is preferably not larger than 0.4, more preferably in the range of 0 to 0.3, and most preferably in the range of 0 to 0.1. In the core/shell structure shown in Figures 2(a) and 2(b), the shell may have two or more layered structure in which the silver bromide content is gradually decreased from the surface to the center of the grain. The difference in the silver bromide content between the core and the shell is preferably not more than 70 mol %, and more preferably in the range of 3 to 35 mol %. In the case that the difference is large, the core may be dissolved at the stage of the shell formation to degrade the shape of the tabular grain.

The shell has a silver iodide content preferably not more than 20 mol %, and more preferably in the range of 0.1 to 10 mol %. The silver iodide content preferably is gradually decreased from the surface to the center of the grain. The silver iodide is preferably localized at a layer of 10 atoms (preferably 5 atoms) from the surface of the grain. The silver iodide is preferably uniformed distributed on the major faces of the grain. The distribution of the silver iodide content preferably is substantially uniform in each of the grains. The shell preferably contains SCN^- in an amount of not less than 0.1 mol %, and more preferably 1 to 50 mol %. The ion of SCN^- is preferably localized at a layer of 10 atoms (preferably 3 atoms) from the surface of the grain. The ion of SCN^- is preferably uniformed distributed on the major faces of the grain. The distribution of the content of the SCN^- ion preferably is substantially uniform in each of the grains.

The term "substantial uniform" means that the distribution coefficient is not larger than 0.4, preferably in the range of 0 to 0.3, and more preferably in the range of 0 to 0.1.

The above-mentioned core/shell structure has various advantages. For example, the silver halide grains substantially (preferably not less than 60 %, more preferably in the range of 75 to 98 %) of silver chloride have a high developing speed. Accordingly, a large amount of a photographic material can be processed per a unit amount of a developing solution. Therefore, the amount of the waste developing solution can be decreased by using the high chloride grains. On the other hand, the silver chloride has a disadvantage that adsorption of a spectral sensitizing dye on the surface of the grain is weak. The van der Waals' force on the silver chloride grain surface is weak because the polarizability of silver chloride is small. In the core/shell structure, the adsorption of the sensitizing dye is enhanced by increasing the silver bromide content in the shell. If necessary, the silver iodide content in the shell can also be increased to further enhance the adsorption of the sensitizing dye. Since the silver bromide and iodide can be localized at the surface or the near surface of the grain, the maximum effect can be obtained by a small amount of silver bromide or iodide. Further, the silver bromide or iodide at the surface of the grain has another effect of decreasing the solubility of the silver halide at the surface of the grain. The occurrence of fog can be reduced by decreasing the solubility. The fog is caused when an emulsion is subjected to a chemical sensitization or when the emulsion or a photographic material is preserved. The above-mentioned surface character of the core/shell grain is similar to conventional AgBrI grain systems.

When an initial developing speed is increased, discrimination between a latent image and a fog speck is weakened to reduce the sensitivity and increase the fog. On the other hand, the above-mentioned influences are small when a later developing speed is increased. The above-mentioned grains accelerate the later developing speed to cause the above-mentioned influences scarcely.

In the grains prepared according to the present invention, the most (preferably at least 60 %, more preferably 80 to 100 %, and most preferably 95 to 100 %) of the grain surface has {100} faces. The polarizability of the {100} face is larger than that of a {111} face. The surface of the {100} face consists of silver ion and halide ion. On the other hand, the surface of the {111} face merely consists of halide ion. Accordingly, the Heitler-London's dispersing power and the induced dipole moment of the {100} face are larger than those of the {111} face. The adsorption of a sensitizing dye is enhanced in the {100} face. Therefore, the amount of silver bromide or iodide on the surface of the grain can be reduced, compared with the conventional {111} face system.

European Patent Publication No. 0,534,395A1 describes in more detail that the adsorption of the spectral sensitizing dye on the {100} face is stronger than that on the {111} face. The van der Waals' forces between the {100} and the {111} face can easily be compared by the dielectric constants parallel to the faces. The dielectric constant of the {100} face and that of the {111} face can be measured by forming a condenser of a single silver halide crystal. At the measurement, the ionic conductive elements of the single silver halide crystal can be removed by increasing the measuring wavelength. Alternatively, the dielectric constant can be obtained from a reflectivity of light, which is transparent through clean {100} and

{111} faces of a single silver halide crystal. The reflectivity of light (n) has a relation to the dielectric constant (ϵ) within a high wavelength region as $\epsilon = n^2$.

The silver iodide in the surface layer can be introduced by a simultaneous mixing method using a silver salt solution and a halide solution. The silver iodide can also be introduced by addition of a halide solution only after the grain growth. The latter method is preferred, since a small amount of silver iodide can effectively be used because the silver iodide can be localized on the surface of the grain.

In the formation of the grain shown in Figure 2(b), the layer of AgX_6 should be uniformly formed on the whole surface of the tabular grains. In this case, a high supersaturated amounts of a silver salt solution and a halide solution and/or a high supersaturated amount of a halide solution is added to the tabular grains. The conditions at the addition such as the addition rates can be experimentally determined by analyzing the structures of the halide compositions in the formed grains.

The structure of the grain can be analyzed by scanning a sectioned tabular grain with an electron beam to detect an emission (e.g., characteristic X-rays) of a halogen atom at each parts of the section (scanning electron microscope analysis). The structure can also be analyzed by a secondary ion mass spectroscopy. The analyzing methods are described in Journal of Japan Photographic Society, volume 53, pages 125 to 131 (1990).

When the feed rate of the silver salt solution or the halide solution of AgX_6 is high, the formation of the AgX_6 is not uniform in each of the grains. Further, the distribution of silver iodide on the surface of the grain is also not uniform. In this case, the addition is preferably conducted through a porous substance, more preferably through a hollow tube type elastomeric rubber porous membrane placed in a reaction solution (described in Japanese Patent Provisional Publication Nos. 3(1991)-21339, 4(1992)-193336, 4(1992)-229852, and Japanese Patent Application No. 4(1992)-240283). A uniformly mixing method (disclosed in Japanese Patent Provisional Publication No. 4(1992)-283741 and Japanese Patent Application No. 4(1992)-302605) is also available. The porous substance and the uniformly mixing method are preferably used in combination.

The grains shown in Figures 2(a) and 2(b) are preferably formed under the conditions that the chloride concentration is not less than 10^{-3} mol per liter and more preferably in the range of $10^{-2.5}$ to 10^{-1} mol per liter. Silver halide grains of other structures are also preferably formed under the above-mentioned chloride conditions. The conditions for the formation of the tabular grains of the present invention are analogous to those for the formation of cubic grains. The above-mentioned chloride conditions are analogous to the chloride conditions for the formation of the cubic grains. The extra amount of the chloride ion can function as an agent for adjusting crystal habits.

Figures 3a and 3b are micrographs showing tabular silver halide grains of the present invention. The tabular grains have the silver chloride content of not less than 99.5 %. The grains are cooled to -100 °C or less, and are observed by a transparent electron microscope. As is shown in the figures 3a and 3b, dislocation lines are observed in the grains.

The contents of other ions and additives may differ at the gap of the tabular grains. Examples of the ions and additives include sulfur, selenium, tellurium, SCN^-, $SeCN^-$, $TeCN^-$, CN^-, a metal ion other then Ag^+ and a complex of a metal ion with a ligand (e.g., X^- ligand, CN^- ligand, isocyano, nitrosyl, thionitrosyl, amine, hydroxyl). The difference in the content at the gap interface is preferably in the range of 0.1 to 100 mol %, more preferably in the range of 1 to 100 mol %, and most preferably in the range of 10 to 100 mol %. Examples of the metal ions other than Ag^+ include the metal ions of the VIII group in the periodic table and metal ions of Cu, Zn, Cd, In, Sn, Au, Hu, Pb, Cr and Mn.

The above-mentioned ions can be doped in the whole of the silver halide grains. The ions can also be doped at a specific part of the grains. The ions can further be doped at a locarized area within 0.1 μm from the surface of the grains. The concentration of the doped ion is preferably in the range of 10^{-8} to 10^{-1} mol per 1 mol of silver halide, and more preferably in the range of 10^{-7} to 10^{-2} mol per 1 mol of silver halide.

Examples of the dopant ions and the doping methods are described in Research Disclosure, volume 307, item 307105 (November, 1989), U.S. Patent Nos. 5,166,045, 4,933,272, 5,164,292, 5,132,203, 4,269,927, 4,847,191, 4,933,272, 4,981,781, 5,024,931, Japanese Patent Provisional Publication Nos. 4-(1992)-305644, 4(1992)-321024, 1(1989)-183647, 2(1990)-20853, 1(1989)-285941 and 3(1991)-118536.

The process for the preparation of tabular grains and the structure of the grains are described in Japanese Patent Provisional Publication Nos. 5(1993)-313273, 5(1993)-281640, Japanese Patent Application Nos. 5(1993)-96250, 5(1993)-248218, 5(1993)-264059, 5(1993)-117624 and 4(1992)-214109. The process and the structure are also described in the above-mentioned documents about the uniformly mixing methods.

At the grain growth or the growth of the layer of AgX_6, previously formed fine silver halide grains can be used. The fine grains preferably have a diameter of not more than 0.2 μm, and more preferably in the range of 0.02 to 0.1 μm. Tabular grains can be grown preferentially along the direction of edges by addition of the fine grains, compared with the addition of ions. The addition of the fine grains is also preferably used to form tabular grains of a high aspect ratio within a broad chloride content range and pH range. The chloride content is preferably in the range of 10-1 to 10-3 mol per liter. The pH is preferably in the range of 3 to 8. The temperature is preferably in the range of 30 to 90 °C.

At the stage of the grain growth, the agent for the formation of a {100} face can be used. An agent for the formation of a {111} face may be used in combination. These agent for adjusting crystal habit decreases the silver potential at the formation of nuclei by not less than 10 mV, and preferably by 30 to 200 mV. The above-mentioned embodiment (b) of the structure can easily be formed using the agents.

Examples of the agents are described in U.S. Patent Nos. 4,399,215, 4,414,306, 4,400,463, 4,713,323, 4,804,621, 4,783,398, 4,952,491, 4,983,508, Journal of Imaging Science, volume 33, page 13 (1989), volume 34, page 44 (1990) and Journal of Photographic Science, volume 36, page 182 (1988).

The grains of the invention are mainly covered with {100} faces. Accordingly, an adsorbing group of gelatin (e.g., methionine) is strongly adsorbed on silver ion on the surface of the grain. Therefore, the adsorption of photographic additives such as a spectral sensitizing dye and an antifogging agent might be inhibited by gelatin. In this case, the methionine content in gelatin used as a dispersing agent is preferably adjusted. In more detail, the average methionine content in gelatin used in emulsion layer of a photographic material is preferably in the range of 0 to 50 µmol/g, and more preferably in the range of 3 to 30 µmol/g.

Besides the process of the present invention, the gap of the halide composition is formed by the following processes.

i) The nuclei formation and the ripening is conducted at the area of the {100} face formation, and then the grain growth is conducted at the area of the {111} face formation.

ii) The nuclei formation and the ripening is conducted at the area of the {111} face formation, and then the grain growth is conducted at the area of the {111} face formation.

iii) The nuclei formation and the ripening is conducted at the area of the {111} face formation, and then the grain growth is conducted at the area of the {100} face formation.

The process ii) forms {111} twinned crystals (mainly single twinned crystals and paralleled double twinned crystals). The process iii) forms {100} twinned crystals. The conditions of the process iii) usually form edge dislocation, which does not cause tabular grains. Accordingly, it seems that the edge dislocation itself is not the cause of the formation of the tabular grains.

The grain growth along the direction of edges can be observed by adding and growing silver halide layers having different iodide contents (difference: 0.5 to 3 mol %) and then observing the low temperature luminescence as is described in Journal of Imaging Science, volume 31, pages 15 to 26, (1987), or directly observing the gap interface of the iodide content with a low temperature transparent electron microscopy. For example, embodiments shown in Figures 4(a), 4(b) and 4(c) can be observed.

Epitaxial grains can be formed from the obtained silver halide grains. Further, grains having dislocation lines inside the grains can be formed by using the obtained grains as grain nuclei. Further, the obtained grains can be used as substrate of other grains, which are formed by forming silver halide layer on the substrate. The halide composition of the layer is different from that of the substrate. The other various silver halide grains can be formed from the grains of the present invention.

A speck of chemical sensitization is usually introduced into the silver halide grains. The place and number (per cm^2) of the chemical sensitization specks are preferably adjusted. The adjustment is described in Japanese Patent Provisional Publications No. 64(1989)-74540, No. 1(1989)-201651, No. 2(1990)-838, No. 2(1990)-146033 and No. 3(1991)-121445 and Japanese Patent Application No. 3(1991)-73266, No. 3(1991)-140712 and No. 3(1991)-115872.

A shallow internal latent image emulsion can be prepared by using the tabular grains as the core. A core/shell emulsion can also be prepared. These emulsions are described in Japanese Patent Provisional Publications No. 59(1984)-133542 and No. 63(1988)-151618, and U.S. Patents No. 3,206,313, No. 3,317,322, No. 3,761,276, No. 4,269,927 and No. 3,267,778.

The silver halide emulsion prepared by the present invention can be mixed with one or more other emulsions. The mixing ratio of the emulsion of the invention to other emulsions can be appropriately arranged within the range of 1.0 to 0.01.

There is no specific limitation with respect to additives, which are used from grain formation to emulsion coating. The amount of the photographic additives is preferably in the range of 10^{-8} to 10^{-1} mol per 1 mol of silver halide. Examples of the additives include silver halide solvents, doping agents for silver halide grains (e.g., metal compounds of the group VIII or other metals, chalcogen compounds and SCN compounds), dispersing agents, antifogging agents, spectral sensitizing dyes (e.g., blue, green, red, infrared, panchromatic or orthochromatic sensitizers), supersensitizers, chemical sensitizers (e.g., sulfur sensitizers, selenium sensitizers, tellurium sensitizers, gold or other noble metals such as metals of the group VIII sensitizers, phosphor compounds, rhodan compounds or reduction sensitizers), fogging agents, emulsion precipitating agents, surface active agents, hardening agents, dyes, color image forming agents, additives for color photography, soluble silver salt, latent image stabilizer, developing agents (e.g., hydroquinone compounds), agents for preventing pressure desensitization and matting agents. Two or more additives (e.g., chemical sensitizers) can be used in combinations.

The silver halide grains and emulsion of the present invention are available in various conventional photographic materials. Examples of the photographic materials include black and white photographic materials (e.g., X-ray sensitive materials, light-sensitive materials for printing, photographic papers, negative films, microfilms, direct positive light-sensitive materials, ultrafine-grain dry light-sensitive materials (for LSI photomask, shadow mask or liquid crystal mask) and color photographic materials (e.g., negative films, color photographic papers, reversal films, direct positive color light-sensitive materials, silver dye bleaching photographic materials). The silver halide emulsion is also available in diffusion transfer light-sensitive materials (e.g., color dye diffusion transfer element, silver salt diffusion transfer element), thermal developable (black and white or color) light-sensitive materials, high density digital recording light-sensitive materials and holography light-sensitive materials.

In the photographic material, the coating amount of silver is preferably not less than 0.01 g/m^2. There is no specific limitation with respect to the structure of the photographic material (e.g., the layered structure, the molar ratio of silver to coloring agents, the silver amounts in the layers), the conditions for light exposure and development, apparatus for preparing the photographic material and dispersing methods of additives. Various conventional structures, additives, methods, apparatus and conditions are available.

The conventional structures, additives, methods, apparatus and conditions are described in Research Disclosure, volume 176, item 17643 (December 1978), and volume 307, item 307105 (November 1989); Duffin, Photographic Emulsion Chemistry, Focal Press, New York (1966); E.J. Birr, Stabilization of Photographic Silver Halide Emulsions, Focal Press, London (1974); T.H. James, The Theory of Photographic Process, fourth edition, Macmillan, New York (1977); P. Glafkides, Chimie et Physique Photographiques, fifth edition, Edition de l'usine Nouvelle, Paris (1987), and second edition, Paul Montel, Paris (1957); V.L. Zalikman et al., Making and Coating Photographic Emulsion, Focal Press (1964); K.R. Hollister, Journal of Imaging Science, volume 31, pages 148 to 156 (1987); J.E. Maskasky, Journal of Imaging Science, volume 30, pages 247 to 254 (1986), volume 32, pages 160 to 177 (1988), volume 33, pages 10 to 13 (1989); Frieze et al. Die Grundlagen Der Photographischen Prozesse Mit Silverhalogeniden, Akademische Verlaggesellschaft, Frankfurt (1968); Journal of Japan Chemical Society, pages 18 to 27, December (1984); and Journal of Japan Photographic Society, volume 49, pages 7 to 12 (1986), volume 52, pages 144 to 166 (1989), volume 52, pages 41 to 48 (1989).

The photographic materials are also described in Japanese Patent Provisional Publications No. 58(1983)-113926, No. 58(1983)-113927, No. 58(1983)-113926, No. 59(1984)-90841, No. 58(1983)-111936, No. 62(1987)-99751, No. 60(1985)-143331, No. 60(1985)-143332, No. 61(1986)-14630, No. 62(1987)-6251, No. 63(1988)-220238, No. 63(1988)-151618, No. 63(1988)-281149, No. 59(1984)-133542, No. 59(1984)-45438, No. 62(1987)-269958, No. 63(1988)-305343, No. 59(1984)-142539, No. 62(1987)-253159, No. 62(1987)-266538, No. 63(1988)-107813, No. 64(1989)-26839, No. 62(1987)-157024, No. 62(1987)-192036, No. 1(1989)-297649, No. 2(1990)-127635, No. 1(1989)-158429, No. 2(1990)-42, No. 2(1990)-24643, No. 1(1989)-146033, No. 2(1990)-838, No. 2(1990)-28638, No. 3(1991)-109539, No. 3(1991)-175440, No. 3(1991)-121443, No. 2(1990)-73245, No. 3(1991)-119347, U.S. Patents No. 4,636,461, No. 4,942,120, No. 4,269,927, No. 4,900,652, No. 4,975,354, European Patent Publication No. 0355568A2, and Japanese Patent Applications No. 2(1990)-326222, No. 2(1990)-415037, No. 2(1990)-266615, No. 2(1990)-43791, No. 3(1991)-160395, No. 2(1990)-142635, No. 3(1991)-146503 and No. 4(1992)-77261.

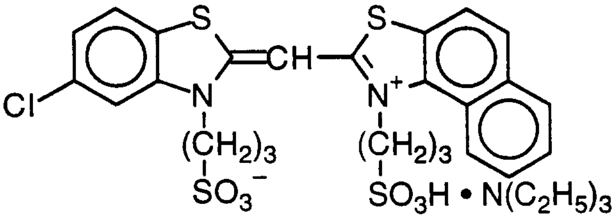
The silver halide emulsion of the present invention is advantageously used in photographic materials disclosed in Japanese Patent Provisional Publications No. 62(1987)-269958, No. 62(1987)-266538, No. 63(1988)-220238, No. 63(1988)-305343, No. 59(1984)-142539, No. 62(1987)-253159, No. 1(1989)-131541, No. 1(1989)-297649, No. 2(1990)-42, No. 1(1989)-158429, No. 3(1991)-226730, No. 4(1992)-151649, Japanese Patent Application No. 4(1992)-179961 and European Patent Publication No. 0508398A1.

EXAMPLE 1

A gelatin solution (comprising 1.2 l of water, 22 g of a deionized alkaline treated gelatin (EA-Gel) having methionine content of 48 µmol/g and 0.5 g of NaCl, and having pH of 4.0 adjusted with HNO_3) was placed in a reaction vessel. To the solution while stirring at 30 °C, 100 ml of Ag-1 solution (containing 20 g of silver nitrate, 0.6 g of a low molecular weight gelatin (2MGel, average molecular weight: 20,000) and 0.2 ml of 1N solution of HNO_3) and X-1 solution (containing 7 g of NaCl and 0.6 g of the low molecular weight gelatin (2MGel) in 100 ml) were simultaneously added at the same feed rate of 50 ml per minute for 30 seconds to form silver chloride nuclei. To the nuclei, X-2 solution (containing 1.4 g of KBr and 0.8 g of the low molecular weight gelatin (2MGel) in 100 ml, bromide content: 100 %) was added through a hollow tube type elastomeric rubber porous membrane (number of the pores: 10,000, diameter of the opened pore at the addition: 0.1 mm). After the mixture was heated to 40 °C, the Ag-1 solution and the X-1 solution were simultaneously added to the mixture at the feed rate of 50 ml per minute for 90 seconds to form nuclei of AgCl|AgBr|AgCl. After the mixture was adjusted to pH 5.0 using 1N NaOH solution, an aqueous solution of NaCl (containing 2.1 g of NaCl) was added to the mixture. The resulting mixture was heated to 70 °C for 15 minutes.

After the emulsion was ripened for 15 minutes, the Ag-1 solution and the X-1 solution were simultaneously added to the emulsion at the initial feed rate of 10 ml per minute and at pCl of 1.45 for 47 minutes while the feed rate is linearly accelerated at 0.1 ml per minute. The emulsion was ripened for 8 minutes. The halide composition of the added solution was about $AgCl_{0.994}Br_{0.006}$. The Ag-1 solution and X-3 solution (containing 4.2 g of KBr and 5.0 g of NaCl in 100 ml, bromide content: about 29 mol %) were added to the emulsion at the feed rate of 50 ml per minute for 1 minute through a hollow tube type elastomeric rubber porous membrane. Further, the Ag-1 solution and X-4 solution (containing 8.4 g of KBr and 2.9 g of NaCl in 100 ml, bromide content: about 59 mol %) were added at the feed rate of 40 ml per minute for 1 minute through the porous membrane. Furthermore, X-5 solution (containing 20 g of KI in 100 ml) was added at the feed rate of 40 ml per minute for 12 seconds. After the emulsion was ripened for 3 minutes, the emulsion was cooled to 40 °C. The following sensitizing dye (amount: 70 % of the saturated adsorbed amount) was added to the emulsion. After the emulsion was stirred for 7 minutes, a precipitating agent is added to the emulsion. The emulsion was cooled to 28 °C, and adjusted to pH 4.0 to effect precipitation. The precipitated emulsion was washed with water. A gelatin solution was added to the emulsion at 38 °C to disperse the emulsion again. The emulsion was adjusted to pH 6.1 and pCl 2.8.

(Sensitizing dye)



A part of the emulsion was sampled, and a replica of the grain of the emulsion was prepared. The replica was observed by a transparent electron microscope (TEM). As a result, 93 % of the grain population projected area was accounted for by tabular grains having {100} major faces, a rectangular shape and an aspect ratio of not less than 3. The average grain size of the tabular grains was 1.4 µm. The average aspect ratio of the grains was 6.2. The distribution coefficient of the grain size (standard deviation of the grain size distribution per average grain size) was 0.2.

The experiment was repeated 10 times. The distribution coefficient in the experiments about the average grain size and the average aspect ratio was not more than 0.03.

COMPARISON EXAMPLE 1

The procedures of the Example 1 were repeated except that Ag-2 solution (containing 2 g of $AgNO_3$ in 100 ml) and X-21 solution (containing 1.4 g of KBr in 100 ml) were simultaneously added to the emulsion at the feed rate of 62 ml per minute (added amount: 40 ml) in place of the addition of the X-2 solution. Accordingly, the structure of the halide composition in the obtained grains is the same as that of the grains obtained in the Example 1.

A replica of the grain was observed by a transparent electron microscope (TEM). As a result, 90 % of the grain population projected area was accounted for by tabular grains having {100} major faces, a rectangular shape and an aspect ratio of not less than 3. The average grain size of the tabular grains was 1.37 µm. The average aspect ratio of the grains was 6.0. The distribution coefficient of the grain size was 0.23.

The experiment was repeated 10 times. The distribution coefficient in the experiments about the average grain size and the average aspect ratio was 0.05. Accordingly, the results of the Example 1 is superior to those of the Comparison example 1 with respect to the reproducibility.

COMPARISON EXAMPLE 2

The procedures of the Comparison Example 1 were repeated except that X-32 solution (containing 7 g of NaCl in 100 ml) was used in place of the X-3 solution and the X-4 solution and the addition of the X-5 solution was omitted. The surface of the obtained grains consists of silver chloride. The halide composition of the obtained grain was $AgCl_{0.994}Br_{0.006}$.

A replica of the grain was observed by a transparent electron microscope (TEM). As a result, 90 % of the grain population projected area was accounted for by tabular grains having {100} major faces, a rectangular shape and an aspect ratio of not less than 3. The average grain size of the tabular grains was 1.4 µm. The average aspect ratio of the grains was 6.1. The distribution coefficient of the grain size was 0.24.

The emulsions obtained in the Example 1 and the Comparison Example 2 were heated to 55 °C. The emulsions were adjusted to pCl 2.2 by addition of NaCl solution. Hypo (2.5×10^{-5} mol per 1 mol of silver halide) and chloroauric acid (10^{-5} mol per 1 mol of silver halide) were added to the emulsions. After the emulsion was ripened, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (3×10^{-3} mol per 1 mol of silver halide) was added to the emulsions as an antifogging agent. The temperature of the emulsions was kept at 40 °C.

To the sensitized emulsions, a viscous agent and a coating aid were added. Each of the emulsions was coated on a TAC base with a protective layer. The emulsions were dried to obtain a coated samples A (Example 1) and B (Comparison Example 1).

The coated samples were exposed to light through a minus blue filter (transparent to light of 520 nm or more) for 10^{-2} second. The samples were developed, stopped, fixed, washed with water and dried. The photographic characteristic (sensitivity value per graininess) of each samples was determined. As a result, the characteristic of the Example 1 was 100, while that of the Comparison Example 1 was 52. Accordingly, the grains of the present invention shown in the Figure 2(a) prepared in the Example 1 are superior to the grains prepared in the Comparison Example 1.

The sample A was sectioned. The sectioned face was analyzed with a scanning electron microscope. As a result the surface of a tabular grain was uniformly covered with a high silver bromide layer (thickness: about 0.02 µm). Further, silver iodide is also uniformly present on the surface of the grain. The distribution coefficient of the iodide content in the grain was not more than 0.15. The distribution coefficient of the iodide content between the grains was also not more than 0.15. Further, the distribution coefficient of the bromide content between the grains was not more than 0.15.

EXAMPLE 2

The procedures of the Example 1 were repeated except that a previously prepared silver chloride fine grain emulsion (average grain size: 0.06 µm, the number ratio of twinned crystals and grains having a dislocation line: 0.1 % or less) was added in place of the addition of the Ag-1 solution and X-1 solution (for 47 minutes while the feed rate is linearly accelerated at 0.1 ml per minute). First, 0.15 mol of the fine grain emulsion was added. After 10 minutes, remaining 0.366 mol of the fine grain emulsion was added to the mixture. The resulting emulsion was ripened for 20 minutes.

The average grain size of the obtained grains was 1.48 µm. The average aspect ratio was 7.3. The distribution coefficient of the grain size was 0.2.

The emulsion was sensitized in the same manner as in the Example 1. A coated sample C was prepared, exposed to light and developed in the same manner as in the Example 1. As a result, the photographic characteristic (sensitivity value per graininess) of the sample C was 105 while that of the Example 1 was 100. Accordingly, the result of the Example 2 was superior to that of the Example 1.

Claims

1. A process for the preparation of a silver halide emulsion comprising silver halide grains dispersed in a dispersing medium, wherein the process comprises steps of:

(1) forming host silver halide nuclei;

(2) adding a halide solution to the silver halide nuclei to form a crystal defect which gives rise the formation of tabular grain, by forming at least one gap interface of halide composition in the nuclei by a halogen conversion reaction, wherein a difference in chloride content or bromide content between the halide composition of the host silver halide nuclei and the halide composition of the

halide solution is in the range of 10 to 100 mol % or a difference in iodide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 5 to 100 mol %; and

(3) growing silver halide grains preferentially along the direction of edges of the grains to form tabular grains having an aspect ratio of not less than 1.5 and {100} major faces.

2. The process as claimed in claim 1, wherein the process further contain a step of:

(4) forming a shell on the tabular silver halide grains formed at the step (3) to form grains having a core/shell structure having the tabular silver halide grains as the core.

3. The process as claimed in claim 2, the core grains formed at the step (3) are high chloride grains having an average silver chloride content of not less than 60 mol %, and the shell formed at the step (4) has a silver bromide content of not less than 30 mol %, and the ratio of the silver chloride content in the shell to the silver chloride content in the core is not larger than 0.8.

4. The process as claimed in claim 2, wherein the shell is substantially uniformly formed on the {100} major faces of the core grains, and the shell has a thickness in terms of three or more atoms.

5. The process as claimed in claim 1, wherein the tabular silver halide grains formed at the step (3) have an average thickness of not more than 0.5 μm, an average diameter of not more than 10 μm and a rectangular projected shape.

6. The process as claimed in claim 1, wherein the difference in chloride content or bromide content between the halide composition of the host silver halide nuclei and the halide comosition of the halide solution is in the range of 30 to 100 mol % or the difference in iodide content between the halide composition of the host silver halide nuclei and the halide composition of the halide solution is in the range of 10 to 100 mol %.

FIG. 1

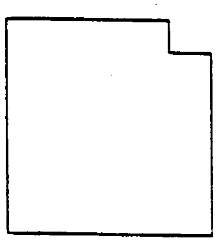


FIG. 2

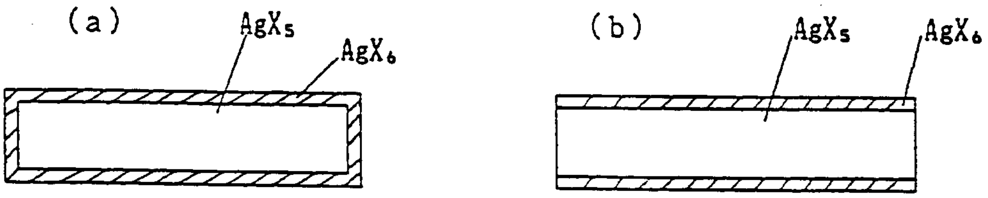
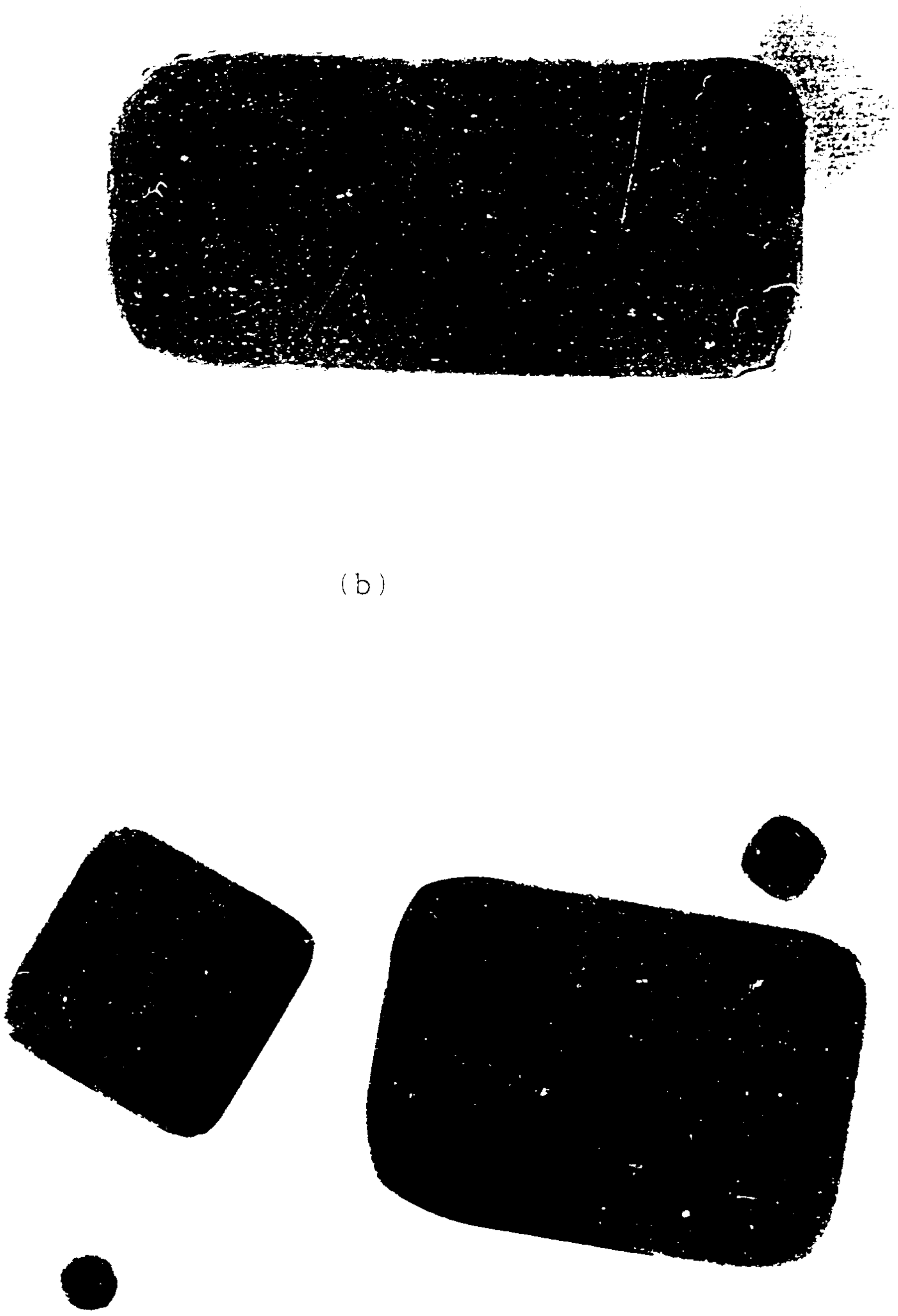


FIG. 3



(a)

(b)

FIG. 4